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### COMPLETE SPECIFICATION

#### Method of producing Acrylic and Methacrylic Esters

We, NAUCHNO-ISSLEDOVATELSKY INSTITUT MONOMEROV DLYA SINTETICHESKOGO KAUCHUKA of Tutaevskoe shosse, Yaroslavl, Union of Soviet Socialist Republics, a Corporation organized under the laws of the Union of Soviet Socialist Republics, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to esters of  $\alpha,\beta$  unsaturated acids and methods of producing the same. More particularly it relates to the production of acrylic and methacrylic esters of higher monohydric and polyhydric alcohols and amino-alcohols.

Herein the term "lower" is used with reference to a molecule or a radical having either 1 or 2 carbon atoms and the term "higher" is used with reference to a molecule or a radical having from 4 to 16 carbon atoms.

The following principal methods of producing acrylate and methacrylate esters of higher alcohols are known: (1) esterification of alcohols with acids or their acid chlorides; (2) transesterification of lower alkyl esters with higher alcohols.

The best and most widely applied method is that of transesterification, which is distinguished by easily available and cheap raw material, simplicity of the process and high yields of product monomers. The process consists in heating a mixture of a higher alcohol or amino-alcohol with an excess of a lower alkyl ester of an unsaturated acid in the presence of a transesterification catalyst and polymerization inhibitor, the lower alcohol formed being simultaneously removed from the reaction mixture. As catalysts in the process

there have been used various acids (e.g. sulphuric acid and p-toluenesulphonic acid), alkali metals and their alcoholates, as well as the alcoholates of titanium and aluminium. In the production of esters of amino-alcohols only catalysts of a basic (alkaline) character have been used.

The method of producing higher alkyl and amino alkyl esters of acrylic and methacrylic acids by transesterification of their lower alkyl esters, the above catalysts being employed, suffers from a number of disadvantages. In the presence of acid catalysts, e.g. concentrated sulphuric acid and p-toluene-sulphonic acid, the reaction proceeds very slowly, requiring up to 10 hr or more for completion. As a consequence of lengthy heating in the presence of strong acids a considerable amount of the initial and final esters of unsaturated acids polymerize and form resins in spite of the presence of effective inhibitors. The process must be carried out in special acid-resistant apparatus and before isolation of the product higher unsaturated esters, the acid in the reaction mixture must be neutralized. Yields of higher alkyl esters of unsaturated acids thus obtained rarely exceed 80% of theory, while yields of esters of polyhydric alcohols, e.g. polyethylene glycol do not exceed 60—70% of theory.

Alcoholates of alkali metals, e.g. sodium, are the most effective transesterification catalysts, but as a consequence of their high reactivity in the conditions of the process they catalyze a number of side reactions: the addition of alcohols at the double bond, resinification of the reagents and polymerization of the initial and product esters. Sodium alcoholates react with esters to form sodium salts which are precipitated, thus making it more difficult

to isolate the product esters. Since the above side reactions are intensified when the concentration of sodium alcoholate in the reaction mixture is increased and, also since the said alcoholates are consumed in forming sodium salts of unsaturated acids, the entire amount of sodium alcoholate must not be added to the reaction mixture at once but in small portions during the entire process. Because of the great fire and explosion hazard when working with alkali metals and preparing their alcoholates, particular caution must be observed which complicates their application in industry. The speed of transesterification of the lower alkyl acrylates and methacrylates with monohydric alcohols or aminoalcohols containing a primary alcoholic group in the presence of titanium alcoholates is close to that of the reaction in the presence of sodium alcoholates. As the degree of shielding of the hydroxyl group is increased, the rate of the reaction in the presence of titanium alcoholates sharply falls. Thus, in the presence of titanium alcoholates, the rate of transesterification of methyl esters with 2-aminoisopropanols is markedly lower than with 2-aminoethanols, while there is practically no transesterification with 1,3-diaminoisopropanols. The rate of transesterification of methyl acrylate and methyl methacrylate with polyatomic alcohols and amino alcohols is also very low.

When a number of higher alkyl and amino-alkyl esters are isolated by vacuum distillation, the monomers are contaminated with volatile titanium alcoholates. In these cases the reaction products must be preliminarily washed with solutions of sodium or potassium citrate to remove the titanium alcoholates.

Aluminium alcoholates are considerably inferior to the above catalysts in their effectiveness. In their presence the reaction mixture must be boiled for dozens of hours to complete the process, which leads to polymerization of substantial amounts of the initial and final esters.

It is the object of the present invention to provide a method of producing acrylic and methacrylic esters of monohydric and polyhydric alcohols and amino-alcohols in high yields in which the above disadvantages are overcome or reduced to the minimum. The present invention enlarges the assortment of effective catalysts for the processes of transesterification and alcoholysis.

According to the present invention, a method of producing acrylic and methacrylic esters of monatomic and polyatomic alcohols and amino alcohols consists of the transesterification of lower alkyl esters of acrylic or methacrylic acids with monohydric and polyhydric alcohols and amino-alcohols, employing as catalysts in the process alkaline earth metals, such as magnesium and calcium, or the alcoholates of said metals such as mag-

nesium methylate, ethylate or butylate, and calcium ethylate.

The transesterification is preferably carried out in the presence of a free-radical-polymerization inhibitor.

In catalytic effectiveness the alkaline earth metals and their alcoholates are not inferior, as a rule, to the alkali metals and their alcoholates, while at the same time they catalyze side reactions to a considerably less degree. Thus, the alcoholates of magnesium and calcium do not cause resinification and colouring of the products and do not react with esters to form salts even on lengthy boiling of the reaction mixture. Consequently, the alcoholates of the alkaline earth metals can be added to the reaction mixture in a single portion, which simplifies the process. It is also possible to add by degrees to the reaction mixture alcoholates of the alkaline earth metals, e.g. magnesium methylate, in the form of a solution in methanol. The use of the alkaline earth metals and their alcoholates does not require special precautionary measures as is the case when working with flammable and explosive alkali metals and their alcoholates.

When acrylates are prepared by transesterification with the use of magnesium or calcium alcoholates, the side reaction wherein alcohols are added at the double bond although occurs but to a much less degree than when alcoholates of the alkali metals are employed, thus making it possible to produce acrylates in satisfactory yields.

The process is preferably carried out as follows. A mixture of a higher alcohol, a lower alkyl ester of acrylic or methacrylic acid, a free-radical-polymerization inhibitor and an alcoholate of an alkaline earth metal are warmed in a flask connected to a fractionating column, thus distilling off the lower alkanol mixed with an excess of the initial ester. After the formation and distillation of the calculated amount of lower alkanol, the unreacted initial lower ester is distilled off, and the remaining product monomer is purified by vacuum distillation or some other method.

If an alkaline earth metal is used, it is first dissolved in the initial alcohol or amino alcohol by heating in the presence of traces of iodine, then the lower alkyl ester of an unsaturated acid and the inhibitor are added to the alcoholate solution thus obtained, and the reaction is further carried out as described above.

The molar ratio of lower alkyl ester to monohydric alcohol may be from 1.2:1 to 5:1, preferably from 1.5:1 to 3:1. For polyhydric alcohols the ratio is increased as many times as there are alcoholic groups in the molecule. The amount of catalyst is from 0.1 to 10% mol, preferably from 0.5 to 4.0% mol, calculated on the basis of the higher alcohol or amino alcohol used. As polymerization

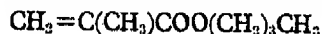
inhibitors there are used phenols, naphthols, aromatic amines, aminophenols, as well as other compounds, such as hydroquinone, di- $\beta$ -naphthol, diphenyl-p-phenylenediamine, p-hydroxydiphenylamine and phenothiazine. The best inhibitors are hydroquinone and phenothiazine in an amount from 0.01 to 3.0% by weight, preferably from 0.1 to 1.0% by weight calculated on the basis of the lower alkyl ester used.

Since the transesterification of lower alkyl methacrylates in the presence of magnesium alcoholates proceeds to almost 100% conversion in a short period of time and without noticeable colouring of the products, the product monomers can be isolated from the reaction products without vacuum distillation. To this end, the reaction products remaining after the excess initial lower ester has been distilled off are freed of inhibitor and catalyst either by washing with a solution of alkali and then with water or by passing through a layer of adsorbent. As a result, methacrylates of higher monohydric and polyhydric alcohols and amino-alcohols are obtained in high yields in the form of colourless or slightly coloured liquids which, according to their constants, results of analysis and polymerizing power, do not differ to any marked extent from specimens isolated by vacuum distillation.

The process of the present invention is illustrated by the following Examples (in which temperatures are given in °C.).

#### EXAMPLE 1.

Preparation of n-butyl methacrylate.



(a) In a flask fitted with a thermometer and a device for adding the catalyst connected to a fractionating column are placed 74.1 g (1.0 g. mol) of n-butyl alcohol, 150 g (1.5 g. mol) of methyl methacrylate and 1 g of hydroquinone. The mixture is heated to boiling and 12 ml of an 8.5% solution of magnesium methylate in dry methanol are added over a period of 15 min. The methanol formed during the reaction together with that introduced with the catalyst is distilled off mixed with methyl methacrylate from the top of the column, the temperature of the vapour being 64–66°. The last methanol at the end of the reaction is distilled off at a higher temperature, up to 70–80°. Over a period of two hours there are distilled off 52 g of a mixture containing 39.8 g of methanol which, taking into account the methanol added with the catalyst, corresponds to 97% conversion of the initial butanol. When the reaction products are distilled in vacuum through a short column, there are obtained in addition to the unreacted methyl methacrylate 134.5 g of n-butyl methacrylate (94.7% of theory). B.p. 50°/10 mm;  $n_D^{20}$  1.4230.

(b) In the apparatus described in Example 1a are placed 74 g (1g.mol) of n-butanol, 0.5 g of magnesium turnings and a small crystal of iodine. The mixture is boiled for 10 min, until the magnesium dissolves after which there are added 150 g (1.5 g.mol) of methyl methacrylate in which 1 g of hydroquinone is dissolved and the reaction carried out as described in Example 1a. Over a period of 110 min., there are distilled off 41.3 g of a mixture containing 31.35 g of methanol which corresponds to 98% conversion of the initial n-butanol. When the reaction products are distilled, there are obtained 135.1 g of n-butyl methacrylate (95.3% of theory); b.p. 56–57°/14 mm.

#### EXAMPLE 2.

Preparation of hexadecyl methacrylate.



(a) In the apparatus for transesterification described in Example 1a are placed 72.7 g (0.3 g.mol) of cetyl alcohol (n-hexadecanol), 80 g (0.8 g.mol) of methyl methacrylate, 2g of hydroquinone and 2.5 g of solid magnesium butylate. Within a period of 160 min the reaction proceeds to 98% completion (according to the amount of methanol collected). The unreacted methyl methacrylate is distilled off in vacuum and the residue diluted with an equal volume of ether, washed with 10% sodium hydroxide until the alkaline layer is no longer coloured, and then with water. The organic layer is filtered and the ether distilled off, care being taken not to heat the monomer above 50°. The remaining monomer is held for 20–30 min in vacuum (1–3 mm Hg) to remove traces of ether, methyl methacrylate and water. There are obtained 89.1 g of n-hexadecyl methacrylate (95.6% of theory) in the form of a transparent, slightly coloured oily liquid;  $n_D^{20}$  1.4518.

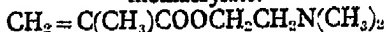
(b) The reaction is repeated under the conditions of Example 2a except that 1 g of  $\alpha$ -nitroso- $\beta$ -naphthol is used as the inhibitor. After completion of the reaction the unreacted methyl methacrylate is distilled off and the residue distilled in a good vacuum. There are thus obtained 87.6 g of n-hexadecyl methacrylate (94.2% of theory); b.p. 154–155°/0.35 mm;  $n_D^{20}$  1.4516. In order to free the monomer of the  $\alpha$ -nitroso- $\beta$ -naphthol impurity it is diluted with ether and washed with 10% sodium hydroxide as described in Example 2a. There are obtained 83.9 g of n-hexadecyl methacrylate (90.1% of theory);  $n_D^{20}$  1.4512; m.p. 15.1°.

Found, %: C 77.8, 77.64; H 12.46, 12.54.

Calculated for  $\text{C}_{20}\text{H}_{38}\text{O}_2$ , %: C 77.36; H 12.33.

## EXAMPLE 3.

Preparation of 2-dimethylaminoethyl methacrylate.



- 5 (a) In a flask fitted with a thermometer and connected to a fractionating column are placed 26.7 g (0.3 g.mol) of 2-dimethylaminoethanol, 60 g (0.6 g.mol) of methyl methacrylate, 0.6 g of phenothiazine and 0.5 g of solid magnesium methylete. The mixture is
- 10 boiled, distilling off the methanol formed during the reaction mixed with methyl methacrylate, the vapour temperature being 64.2—66°. Over a period of 40 min, there is distilled off 11.5 g of a mixture containing
- 15 8.6 g of methanol which corresponds to a conversion of 89.6%. In another 20 min at a vapour temperature of 68—80°, 1.4 g of a mixture is distilled off containing 0.6 g of
- 20 methanol. The total amount of methanol collected is 9.2 g (96% of theory). The unreacted methyl methacrylate is distilled off from the transparent colourless reaction mixture under reduced pressure. The residue is distilled in
- 25 vacuum through a short Vigreux column to give 41.1 g of 2-dimethylaminoethyl methacrylate (87.4% of theory); b.p. 69—70°/11 mm;  $n_D^{20}$  1.4396;  $d_4^{20}$  0.9321;  $\text{MR}_D$  44.27.

Found, %: N 8.72, 8.94.

- 30 Calculated for  $\text{C}_8\text{H}_{15}\text{NO}_2$ , %: N 8.91.

Before distilling off the methyl methacrylate, acetic acid may be added to the reaction products in an amount sufficient to neutralize the magnesium methylete.

- 35 **Hydrochloride.** M.p. 122.—122.5° (from benzene). Found, %: N 7.08, 7.15. Calculated for  $\text{C}_8\text{H}_{15}\text{ClNO}_2$ , %: N 7.20.

**Methiodide.** M.p. 137.—137.5° (from acetone). Found, %: N 4.7, 4.83. Calculated for  $\text{C}_8\text{H}_{15}\text{INO}_2$ , %: N 4.91.

- (b) The reaction of 17.8 g (0.2 g.mol) of
- 40 2-dimethylaminoethanol and 40 g (0.4 g.mol) of methyl methacrylate in the presence of 0.6 g of solid calcium ethylate and 0.4 g of phenothiazine is carried out according to the method described in Example 3 a. After two
- 45 hours, conversion according to the methanol collected amounts to 93% of theory. When the reaction products are distilled in vacuum there are obtained 26.4 g of 2-dimethylaminoethyl methacrylate (84.1% of theory);
- 50 b.p. 69—70/11 mm;  $n_D^{20}$  1.4395.

- By the same method methyl acrylate or methyl methacrylate is subjected to transesterification with the appropriate amino alcohols in the presence of magnesium
- 55 methylete and phenothiazine to give the following amino esters:

2-Dimethylaminoethyl acrylate.



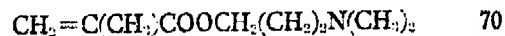
b.p. 61.5—63°/13 mm;  $n_D^{20}$  1.4372;  $d_4^{20}$  0.9406;  $\text{MR}_D$  39.85, calc. 39.65. Found, %: N 9.94; 9.83. Calc. for  $\text{C}_7\text{H}_{13}\text{NO}_2$ , %: N 9.78.

2-Dimethylaminoisopropyl methacrylate.



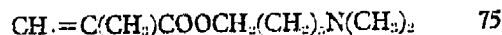
b.p. 80—81°/22 mm;  $n_D^{20}$  1.4345,  $d_4^{20}$  0.9114.  $\text{MR}_D$  48.97, calc. 48.90. Found, %: N 8.29, 8.04. Calc. for  $\text{C}_9\text{H}_{17}\text{NO}_2$ , %: N 8.18.

3-Dimethylaminopropyl methacrylate.



b.p. 80.5°/9mm;  $n_D^{20}$  1.4418;  $d_4^{20}$  0.9258.  $\text{MR}_D$  48.91, calc. 48.90. Found, %: N 8.03, 8.14. Calc. for  $\text{C}_{11}\text{H}_{19}\text{NO}_2$ , %: N 8.18.

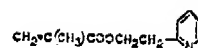
6-Dimethylaminohexyl methacrylate.



b.p. 109—114°/2 mm;  $n_D^{20}$  1.4480;  $d_4^{20}$  0.9106.  $\text{MR}_D$  62.70, calc. 62.74. Found, %: N 6.44, 6.58. Calc. for  $\text{C}_{17}\text{H}_{27}\text{NO}_2$ , %: N 6.56.

## EXAMPLE 4.

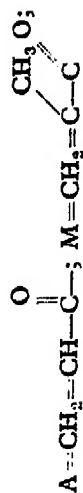
Preparation of 2-(2-pyridyl)-ethyl methacrylate



In the transesterification apparatus are placed 61.6 g (0.5 g.mol) of 2-(2-pyridyl)-ethanol, 100 g (1.0 g.mol) of methyl methacrylate and 0.3 g of hydroquinone. The mixture is heated to 100° and 2 ml of 10% magnesium methylete solution in dry methanol are added. A mixture of methanol and methyl methacrylate is distilled off at 64.5°/66°. During the reaction 1 ml portions of the catalyst solution are added three more times. Over a period of 3 hr 18.9 g of methanol are distilled off; when the methanol added with the catalyst is taken into account this corresponds to a conversion of 96.5%. To the mixture is added 0.6 g of glacial acetic acid to neutralize the magnesium methylete, after which the unreacted methyl methacrylate is distilled off under reduced pressure. The residue is passed through 20 ml of highly basic anionite AB—17 in alkaline form. There are obtained 89.7 g of 2-(2-pyridyl) - ethyl methacrylate (94.1% of theory) in the form of a transparent slightly coloured liquid:  $n_D^{20}$  1.5080. Found, %: N 6.99, 7.08. Calc. for  $\text{C}_{11}\text{H}_{11}\text{NO}_2$ , %: N 7.32. Hydroquinone content 0.0026% by



TABLE I



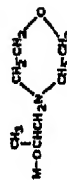
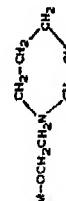
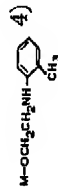
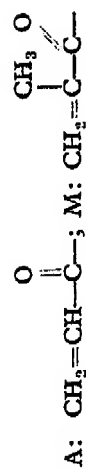
No. of examples	Formula of product monomer	Conditions						Yield, % of theory
		Methyl ester: alcohol (g.mol)	Catalyst	Inhibitor	Duration, min	Conversion, %		
1	2	3	4	5	6	7	8	
9	$M-O-C_{10}H_{21}-n^1)$	1:0.5	$Mg(OC_4H_9-n)_2$	phenothiazine	115	96.2	91.4	
10	$M-OCH_2CH_2N(C_2H_5)_2$	0.9:0.5	$Mg(OCH_3)_2$	phenothiazine	105	98	92.3	
11	$M-OCH(CH_3)CH_2N(CH_2-CH(CH_3)_2)_2$	0.25:0.1	$Mg(OCH_3)_2$	phenothiazine	80	99.2	91.6	
12		0.25:0.1	$Mg(OCH_3)_2$	phenothiazine	—	—	—	
13		1.0:0.5	$Mg(OCH_3)_2$	phenothiazine	100	95.7	90.4	
14	$M-OCH_2CH_2NHC_4H_9-tert. 2)$	1.0:0.5	$Mg(OCH_3)_2$	phenothiazine	150	98	80.5	
15	$M-OCH_2CH_2NH-C_6H_5 3)$	1.1:0.5	$Mg(OCH_3)_2$	diphenyl-p-phenylenediamine	90	99.5	76	
16		0.45:0.15	$Mg(OC_2H_5)_2$	phenothiazine	—	—	78.2	

TABLE 1—Continued

1	2	3	4	5	6	7	8
	$\text{CH}_3$						
17	$\text{M}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	0.3:0.1	$\text{Mg}(\text{OCH}_3)_2$	phenothiazine	45	98	90.8
18	$\text{M}-\text{OCH}(\text{CH}_2\text{N}(\text{CH}_3)_2)\text{CH}_2\text{N}(\text{CH}_3)_2$	0.45:0.20	$\text{Mg}(\text{OC}_2\text{H}_5)_2$	phenothiazine	—	—	83.7
19	$\text{A}-\text{OCH}_2\text{CH}_2\text{NHC}_4\text{H}_9\text{—tert. 5)}$	0.5:0.2	$\text{Mg}(\text{OC}_2\text{H}_5)_2$	phenothiazine	150	68.3	42.1
20	$\text{M}-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{O—M 6)}$	1.45:0.29	$\text{Mg}(\text{OCH}_3)_2$	-nitroso- $\beta$ -naphthol	120	99.0	85.9
21	$(\text{M}-\text{OCH}_2\text{CH}_2)_3\text{N 7)}$	0.5:0.1	$\text{Mg}(\text{OCH}_3)_2$	hydroquinone	55	98.3	94.5
22	$(\text{M}-\text{OCH}_2\text{CH}_2)_2\text{NCH}_3$	0.4:0.1	$\text{Mg}(\text{OCH}_3)_2$	phenothiazine	90	95.5	86
23	$(\text{M}-\text{OCH}_2\text{CH}_2)_2\text{NCH}_2\text{—CH=CH}_2$	0.4:0.1	$\text{Mg}(\text{OCH}_3)_2$	phenothiazine	—	—	88.7
24	$(\text{M}-\text{OCHCH}_3)_2\text{NCH}_3$	0.5:0.1	$\text{Mg}(\text{OC}_4\text{H}_9\text{—n})_2$	phenothiazine	130	97	85.9

<sup>1)</sup> Isolated without distillation by method described in Example 8.

TABLE 2



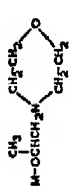
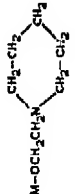
No. of example	Formula of product monomer	B.p. °C/mm Hg	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	Found	Calc.	MR <sub>d</sub>	Found	%N	Calc.
1	2	3	4	5	6	7	8	9		
9	M-O-C <sub>10</sub> H <sub>21</sub> -n <sup>1)</sup>	97-100/1-1.5	1.4420	—	—	—	—	—	—	—
10	M-OCH <sub>2</sub> CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	89/9	1.4445	0.9206	53.57	53.51	7.49	7.56		
							7.57			
11	$\begin{array}{c} \text{CH}_3 \\   \\ \text{M-OCHCH}_2\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)_2)_2 \end{array}$	74-76/1	1.4595	0.9230	66.20	66.43	6.26	6.27		
							6.13			
12		83/0.5	1.4634	1.0156	57.88	57.57	6.60	6.57		
							6.87			
13		78/1	1.4695	0.9806	56.06	55.93	6.95	7.10		
							7.16			
14	M-OCH <sub>2</sub> CH <sub>2</sub> NHC <sub>4</sub> H <sub>9</sub> -tert. <sup>2)</sup>	80-90/10	1.4420	0.9184	53.20	53.17	7.45	7.56		
							7.36			



TABLE 2—Continued

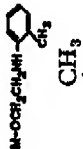

1	2	3	4	5	6	7	8	9
15	M—OCH <sub>2</sub> CH <sub>2</sub> NH—C <sub>6</sub> H <sub>5</sub> <sup>3)</sup>	(M.p. 25—26°) 120—125/1	1.5441	1.0781	—	—	7.10 7.08	6.83
16		120—122/1	1.5410	1.0629	—	—	6.43 6.57	6.39
17	M—OCH <sub>2</sub> CH <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	90.0—91/1	1.4540	0.9291	66.55	66.68	12.43 12.44	12.26
18		70—73/0.4	1.4478	0.9240	62.01	62.06	12.99 13.06	13.07
19	A—OCH <sub>2</sub> CH <sub>2</sub> NHC <sub>4</sub> H <sub>9</sub> —tert. <sup>5)</sup>	79—80/10	1.4413	0.9252	48.83	48.55	8.35 8.28	8.19
20	M—O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O—M <sup>6)</sup>	135—139/1	1.4608	—	—	—	—	—
21	(M—OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N <sup>7)</sup>	—	1.4785	—	—	—	3.88 4.09	3.96
22	(M—OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCH <sub>3</sub>	107—108/0.35	1.4660	1.0300	68.64	68.55	5.38 5.52	5.49
23	(M—OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> —CH=CH <sub>2</sub>	108—110/0.3	1.4725	1.0193	77.36	77.32	5.21 5.13	4.98

TABLE 2—Continued

1	2	3	4	5	6	7	8	9
24	$\begin{array}{c} \text{CH}_3 \\   \\ (\text{M}-\text{OCH}-\text{CH}_2)_2\text{NCH}_3 \end{array}$	108/1	1.4562	0.9882	77.94	77.78	5.22	5.10 4.95

1. Found, %: C 74.57, 74.32; H 11.62. Calc. for  $\text{C}_{14}\text{H}_{26}\text{O}_2$ , %: C 74.30; H 11.58.
2. Hydrochloride. M.p. 97—98° (from ether). Found, %: Cl 16.10, 16.21; N 6.25, 6.27. Calc. for  $\text{C}_{10}\text{H}_{20}\text{ClNO}_2$ , %: Cl 16.03; N 6.31.
3. Hydrochloride. M.p. 127—128° (from ether). Found, %: Cl 14.57, 14.62; N 5.75, 5.88. Calc. for  $\text{C}_{13}\text{H}_{16}\text{ClNO}_2$ , %: Cl 14.71; N 5.79.
4. Hydrochloride. M.p. 137—138° (from ether). Found, %: Cl 13.81, 14.10; N 5.51, 5.59. Calc. for  $\text{C}_{13}\text{H}_{18}\text{ClNO}_2$ , %: Cl 13.90; N 5.48.
5. Hydrochloride. M.p. 131—132° (from ether). Found, %: Cl 17.25, 17.01; N 6.79, 6.76. Calc. for  $\text{C}_{16}\text{H}_{18}\text{ClNO}_2$ , %: Cl 17.10; N 6.75.
6. Found, %: C 58.88, 59.10; H 7.84, 7.98. Calc. for  $\text{C}_{14}\text{H}_{27}\text{O}_3$ , %: C 58.78; H 7.69.
7. Found, %: C 60.90, 60.99; H 7.84, 7.75. Calc. for  $\text{C}_{18}\text{H}_{27}\text{NO}_6$ , %: C 61.17; H 7.70.

## WHAT WE CLAIM IS:—

1. A method of producing acrylic and methacrylic esters of higher (hereinafter defined) monohydric and polyhydric alcohols and amino-alcohols by catalytic transesterification which comprises heating a lower (hereinafter defined) alkyl ester of acrylic or methacrylic acid with a higher monohydric or polyhydric alcohol or amino-alcohol in the presence of an alkaline earth metal or an alcoholate thereof as catalyst.
2. A method according to claim 1 wherein the catalyst is magnesium.
3. A method according to claim 1 wherein the catalyst is a magnesium alcoholate.
4. A method according to claim 3 wherein the catalyst is magnesium methylete, ethylete or butylete.
5. A method according to claim 1 wherein the catalyst is calcium or a calcium alcoholate.
6. A method according to claim 5 wherein the catalyst is calcium ethylete.
7. A method according to any of the preceding claims wherein the amount of catalyst is from 0.1 to 10 mol percent calculated on the basis of the higher alcohol or amino-alcohol.
8. A method according to claim 7 wherein the amount of catalyst is from 0.5 to 4.0 mol percent.
9. A method according to any preceding claim wherein the transesterification is carried out in the presence of a free-radical-polymerization inhibitor.
10. A method according to claim 1 substantially as described herein with reference to any of the Examples.

11. An acrylic or methacrylic ester produced by the method of any of the preceding claims.

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